Configuration interaction studies of the excited states of water*

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(Received 27 December 1974)

We report the results of extensive configuration interaction studies on 16 excited states of water. These states can be accurately described as corresponding to excitation from one of the highest two molecular orbitals ($1b_1$ or $3a_1$) of the ground state into either the $3s$ or one of the three $3p$ Rydberg orbitals. The results provide the most accurate and consistent treatment of these states to date (within 0.1 eV for all known transitions) and form a reliable basis for the assignment of the photon and electron impact spectra of H_2O.

I. INTRODUCTION

The water molecule continues to be the subject of considerable experimental[1-8] and theoretical[9-22] study, still providing surprises and controversy. For example the energy loss feature at 4.6 eV in the electron impact spectra remains a mystery. It was first attributed to the lowest triplet state of water, but numerous theoretical studies[9,10,15,16] have shown conclusively that the lowest vertical transition to a triplet state is >6.5 eV. More recent experiments[2] have observed a well-defined structured feature at 4.6 eV, but this has been shown to be detection of H^- ions produced by dissociative attachment at 6.5 eV incident energy.[2,6] This does not explain the original 4.6 eV feature, however, since the earlier experiments were carried out with incident energies >10 eV, considerably off resonance. Recent observation of photon absorption near 5 eV in supersaturated water vapor[7] may be related to the electron impact feature (observed at incident energies >10 eV).

Over the years there have been numerous theoretical calculations on the ground state of H_2O culminating in the extensive Hartree–Fock and configuration interaction (CI) studies of the Battelle–Ohio State group.[17-19]

The first comprehensive studies of the excited states of water were reported by Hunt and Goddard[9] in 1969 followed by a more complete study[10] in 1971 and 1974. These results were used to make assignments of the various observed transitions and predictions for the locations of many unobserved transitions.[10] However, the wavefunctions in these previous studies were of the Hartree–Fock form, and included electron correlation semiempirically. In this paper we report extensive CI studies on the ground and 16 excited states of H_2O, finding that although Goddard and Hunt[10] arrived at correct assignments in each case, several excitation energies were in error by 0.3 eV or more. Using the present more accurate results along with the previous results on the higher states as a guide, Chutjian *et al.*[23] have searched for the various forbidden transitions of water (by varying incident electron energy and scattering angle) and have assigned most features corresponding to excitation energies below 12 eV. These and other experimental results indicate that nearly all of our excitation energies are accurate to 0.1 eV.

II. CALCULATIONAL DETAILS

The ground state Hartree–Fock (HF) wavefunction is (neglecting spin and antisymmetry)

$$\psi_{HF} = (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2, \quad (1)$$

where the $1b_1$ and $3a_1$ orbitals are the highest and second highest occupied orbitals. The various excited states considered here are single excitations from either of these orbitals into unoccupied orbitals of $3sa_1$, $3pa_1$, $3pb_2$, or $3pb_1$ character. Counting both triplet and singlet spin couplings of the open shell orbitals, this leads to sixteen excited states.

The calculations were carried out with the Dunning[24] contracted [4s2p/2s] Gaussian basis set augmented with one set of diffuse s and p Gaussians on the oxygen atom with an exponent of 0.028.[25] The open-shell HF calculations employed the fully self-consistent technique of Hunt *et al.*[26] as incorporated into the program of Hunt, Hay, and Goddard.[27]

For each state both fully self-consistent Hartree–Fock and improved virtual orbital (IVO) calculations (Hunt and Goddard[9]) were carried out. This allows a comparison of results presented here with the IVO calculations reported earlier by Goddard and Hunt[10] using a more complete basis set.

The CI calculations included all single and double excitations from each occupied orbital (except the $1a_1$) of the HF wavefunction for *each* state. The full (18-function) orbital space of the ground state was used in each case. Selected calculations using a virtual space optimized for the excited states yielded essentially identical results. The sources of error are (1) the lack of correlation and readjustment of the $1a_1$ orbital, (2) the constraint of allowing no higher than double excitations, (3) the lack of additional diffuse functions, and (4) the lack of d basis functions.

Symmetry was used to block diagonalize the CI matrix, and for cases in which several states have the same symmetry, the excited states were found as roots of *one* CI matrix constructed from a configuration list that was a union of the lists for the individual states. This ensures that the energy for each state is an upper bound and yields the best results for the excitation energies.

This procedure leads to between 4000 and 6000 determinants and 2000 to 3000 spin eigenfunctions for the various states.

III. RESULTS AND COMPARISON WITH EXPERIMENT

The energies from our HF and CI calculations are listed in Table I and the excitation energies from the CI calculations are compared with the experimental results in Table II.[28–32]

Five excitation energies have been well established experimentally, namely, $^1B_1(1b_1 \rightarrow 3sa_1)$ at 7.49 eV, $^3A_1(1b_1 \rightarrow 3pb_1)$ at 9.81 eV, $^1A_1(1b_1 \rightarrow 3pb_1)$ at 10.172 eV, $^1B_1(1b_1 \rightarrow 3pa_1)$ at 9.996 eV, and $^1A_1(3a_1 \rightarrow 3sa_1)$ at 9.73 eV. The differences between the calculated and experimental values in these cases are 0.12, −0.07, −0.01, +0.06, and +0.09 eV, respectively. Since the calculated values are within 0.1 eV of the experimental values for the known states, the predicted energies for the other states should be useful in searching for the weaker transitions.

The 4.6 eV feature observed in electron impact studies had been assigned by the experimentalists as a triplet state.[1] Hunt and Goddard[10b] in 1971 found that the vertical excitation energy was at least 6.6 eV and concluded that the 4.6 eV feature did not correspond to excitation of the monomer to an excited state (they suggested the dimer as a possibility).[10b] In 1971, on the basis of CNDO calculations, Claydon *et al.*[11] assigned the 4.5 eV feature as due to $^3B_1$. In 1973, Hosteny *et al.*[15] carried out CI calculations over an extensive region of geometries and showed conclusively that the $^3B_1$ state could not give rise to the 4.5 eV feature.

Our work clearly establishes the $^3B_1$ state to be near 7.2 eV, explaining the feature found recently with electron impact.[4,23] All previous calculations of the $^3B_1$ state[9–16] underestimated the excitation energy by 0.3 to 1.0 eV.

TABLE I. Comparison of Hartree–Fock and configuration interaction energies for the ground and excited states of H_2O.

		Hartree–Fock		Configuration interaction	
Excitation	State	Energy(hartree)	ΔE(eV)	Energy(hartree)	ΔE(eV)
Ground state	$^1A_1$	−76.01114	0.0	−76.13869	0.0
$1b_1 \rightarrow 3sa_1$	$^3B_1$	−75.79080	6.0	−75.87193	7.26
				(−75.87400)	(7.20)
	$^1B_1$	−75.77691	6.37	−75.85907	7.61
				(−75.86074)	(7.56)
$1b_2 \rightarrow 3pb_2$	$^3A_2$	−75.71319	8.10	−75.79558	9.34
	$^1A_2$	−75.70868	8.23	−75.79105	9.46
$1b_1 \rightarrow 3pb_1$	$^3A_1$	−75.69623	8.57	−75.78089	9.79
	$^1A_1$	−75.69381	8.64	−75.76527	10.16
$1b_1 \rightarrow 3pa_1$	$^3B_1$			−75.77141	9.99
	$^1B_1$	−75.68353	8.91	−75.76891	10.06
$3a_1 \rightarrow 3sa_1$	$^3A_1$	−75.71270	8.12	−75.79171	9.44
				(−75.79487)	(9.36)
	$^1A_1$	−75.70116	8.44	−75.77764	9.82
				(−75.78433)	(9.64)
$3a_1 \rightarrow 3pb_2$	$^3B_2$	−75.64236	10.04	−75.73038	11.11
	$^1B_2$	−75.63483	10.24	−75.71718	11.47
$3a_1 \rightarrow 3pb_1$	$^3B_1$	−75.62064	10.63	−75.70230	11.87
	$^1B_1$	−75.61925	10.66	−75.70050	11.92
$3a_1 \rightarrow 3pa_1$	$^3A_1$			−75.70623	11.77
	$^1A_1$	−75.62057	10.63	−75.69471	12.08

TABLE II. Comparison of theoretical and experimental excitation energies (in eV).

Excitation	Upper state	Theoretical CI	Experimental[a]	Best value
$1b_1 \rightarrow 3sa_1$	$^3B_1$	7.26	7.2,[b] 7.0[d]	7.14
	$^1B_1$	7.61	7.4,[c,d] 7.49[e]	7.49
$1b_1 \rightarrow 3pb_2$	$^3A_2$	9.34	9.1,[b] 9.2,[f] 8.9[d]	9.1
	$^1A_2$	9.46	9.1[d]	9.2
$1b_1 \rightarrow 3pb_1$	$^3A_1$	9.74	9.81,[c] 9.80[d]	9.81
	$^1A_1$	10.16	10.14,[g] 10.17,[c] 1,0.172,[e] 10.16[d]	0.17
$1b_1 \rightarrow 3pa_1$	$^3B_1$	9.99	9.98[d]	9.93
	$^1B_1$	10.06	10.01,[b,c,d,f,g] 9.996[e]	10.00
$3a_1 \rightarrow 3sa_1$	$^3A_1$	9.44	9.3[d]	9.35
	$^1A_1$	9.82	9.7,[b,c,d,g] 9.73[e]	9.73
$3a_1 \rightarrow 3pb_2$	$^3B_2$	11.11		11.1
	$^1B_2$	11.47		11.5
$3a_1 \rightarrow 3pb_1$	$^3B_1$	11.87		11.86
	$^1B_1$	11.92	11.91[g,h]	11.91
$3a_1 \rightarrow 3pa_1$	$^1A_1$	11.77		11.8
	$^1A_1$	12.08		12.1

[a]The most accurately determined and assigned numbers are indicated with an underline. In many cases the experimental excitation energies were not assigned by the original authors but are identified by this work as discussed in Sec. III.
[b]Knoop *et al.*, Rev. 4
[c]Trajmar *et al.*, Ref. 1.
[d]Chutjian *et al.*, Ref. 23.
[e]Johns, Ref. 31.
[f]Schulz, Ref. 5.
[g]Skerbele *et al.*, Ref. 3.
[h]Watanabe and Jursa, Ref. 32.

The 7.49 eV feature in the optical spectrum has long been assigned as the $^1B_1(1b_1 \rightarrow 3sa_1)$ state [Mulliken (1935),[29] Price (1936),[30] Johns (1963)[31]], in agreement with our results (calculated energy at 7.61 eV).

Our calculations indicate that the next excited state is $^3A_2(1b_1 \rightarrow 3pb_2)$ at 9.34 eV followed closely by $^1A_2(1b_1 \rightarrow 3pb_2)$ at 9.46 eV and $^3A_1(3a_1 \rightarrow 3sa_1)$ at 9.44 eV. The states in this region have not been well characterized experimentally. Schulz (1960)[5] observed a peak at 9.2 eV with the trapped electron method and Knoop *et al.* (1972)[4] detected a transition at 9.1 eV in a low energy electron impact spectrum. Chutjian *et al.*[23] have recently examined the nine eV region very closely, looking for these states. Their lowest energy loss feature is at 8.9 eV for a scattering angle of 130°. It is not clear which combination of singlet and triplet transitions were observed in the above experiments. On the basis of both our calculations and the experimental results we conclude that the lowest transition is to $^3A_2$ at ~9.1 eV [leading to an error of 0.2 eV in the predicted energy, the largest error for any of the 16 states reported here]. Since the calculated $^3A_2 - {}^1A_2$ splitting is 0.12 eV, we expect the $^1A_2$ state to be at ~9.2 eV. [The electron impact spectra of Chutjian *et al.*[23] does show the lowest peak moving to higher energy by ~0.2 eV as the scattering angle is decreased to 20°.] Just as found for the lower $^{1,3}B_1$ states, no sharp delineation between the $^{1,3}A_2$ states is expected in the electron impact spectrum as the scattering angle is varied. For the A_2 states the distinction is even more difficult since the $^1A_2$ state is

dipole-forbidden and the cross section is expected to decrease for forward (0°) scattering.[33]

Claydon *et al.*[11] suggested that the $^1A_2$ state is responsible for a low intensity feature in the electron impact spectrum at 6.5 eV [Skerbele *et al.* (1969)[3]], an assignment that is clearly incorrect. Yeager *et al.*[16] assigned the 9.1 and 9.2 eV features of Schulz[5] and Knoop *et al.*[4] as due to the $^1A_2$ state.

The other state in this region is $^3A_1(3a_1 \rightarrow 3sa_1)$ calculated at 9.44 eV. The corresponding $^1A_1$ state calculated at 9.82 eV is observed at 9.73 eV; hence using the calculated singlet–triplet spacing and the experimental $^1A_1$ energy we expect the $^3A_1$ state to lie at 9.35 eV and slightly above the $^1A_2$ state. At intermediate scattering angles Chutjian *et al.*[23] find that the nine eV feature moves as high as 9.3 eV, possibly indicating an increased contribution due to the $^3A_1$ state.

The 9.81 eV transition was first observed and identified as a triplet state by Trajmar *et al.* (1971, 1973).[1] Hunt and Goddard (1971)[10b] assigned this as the $^3A_1 \times (1b_1 \rightarrow 3pb_1)$ transition which is in agreement with the CI results. The fact that the excitation is from the nonbonding $1b_1$ orbital is consistent with the sharpness of this transition. Yeager *et al.* (1974)[16] were not able to decide on the assignment of this feature, believing it to be due to either the $^3A_1(1b_1 \rightarrow 3pb_1)$ or $^3B_1(1b_1 \rightarrow 3pa_1)$ state.

The CI results predict the $^3B_1(1b_1 \rightarrow 3pa_1)$ transition to be at 9.99 eV and the corresponding singlet at 10.06 eV. The $^1B_1$ state is well known from electron impact [Chutjian *et al.* (1974)[23]] and optical spectra [Johns (1963)[31]] to lie at 10.00 eV. Thus using the calculated singlet–triplet splitting of 0.07 eV we expect the $^3B_1$ state to be at 9.92 eV. This is consistent with the electron impact spectrum although the $^3B_1$ state is not resolved. The equations of motion calculations[16] place the $^{1,3}B_1 \times (1b_1 \rightarrow 3pa_1)$ states low by ~0.5 eV.

The next excited states are expected to arise from $1b_1 \rightarrow 4sa_1$ and $1b_1 \rightarrow 3d$ (five cases) and had been assigned by the experimentalists[31,34] to the transitions observed at 10.99 and 11.12 eV. However, IVO calculations[10] have placed the $1b_1 \rightarrow 3d$ transitions at ~11 eV and the $1b_1 \rightarrow 4sa_1$ $^{3,1}B_1$ states at 10.51 and 10.65 eV, respectively. The recent electron impact spectra of Chutjian *et al.*[23] show a forbidden transition at 10.41 eV, which is consistent with the $^3B_1$ state, supporting the assignments of Goddard and Hunt.[10]

The $^{1,3}B_2(3a_1 \rightarrow 3pb_2)$ states are calculated to lie at 11.11 and 11.47 eV but have not yet been assigned in the spectra. Claydon *et al.*[11] suggested that the $^1B_2$ state contributes to the energy loss processes in the 8.7–10.0 eV range, clearly an incorrect suggestion. Goddard and Hunt[10] suggested that a shoulder at 11.4 eV in the optical spectrum of Watanabe *et al.*[32] might correspond to the $^1B_2$ transition. This is consistent with our CI results but definite assignment of transitions in the region is difficult without careful isotope studies to eliminate vibrational overtones of nearby strong transitions.

The CI calculations predict the dipole-allowed transitions $^1B_1(3a_1 \rightarrow 3pb_1)$ at 11.92 eV and $^1A_1(3a_1 \rightarrow 3pa_1)$ at 12.08 eV. Both optical[30,32] and electron impact spectra[3] show singlet excitation features at 11.75, 11.91, 12.07, and 12.24 eV of which 11.75, 12.07, and 12.24 correspond to $1b_1 \rightarrow 5d$, $6d$, $7d$, respectively. We believe that the $^1B_1(3a_1 \rightarrow 3pb_1)$ is responsible for at least a major part of the 11.91 eV transition ($1b_1 \rightarrow 5p$ transitions would also be in this region but probably less intense). The $^1A_1(3a_1 \rightarrow 3pa_1)$ transition is probably obscured by the $1b_1 \rightarrow 6d$ transitions at 12.07 eV.

In the last column of Table II we have combined the experimental and theoretical information on these transitions to give a "best value." Where unambiguous experimental information is available, that energy is quoted. Otherwise a corrected theoretical value is used, for example, the $^1B_1(1b_1 \rightarrow 3sa_1)$ state is known from optical spectra to lie at 7.49 eV, indicating the CI calculation is high by 0.12 eV. The error in the calculated $^3B_1$ excitation energy should be essentially the same, providing a "best value" of 7.14 eV (the experimental values range from 7.0 to 7.2 eV).

IV. COMPARISON OF THEORETICAL RESULTS

A. Importance of diffuse basis functions

Before comparing the results for various types of calculations, we will examine the CI calculations for the ground state and the $^{1,3}B_1(b_1 \rightarrow 3sa_1)$ and $^1A_1(3a_1 \rightarrow 3sa_1)$ excited states in three different Gaussian basis sets. The first was the *DZ* valence [4*s*2*p*/2*s*] set[24] (also used in the ground state CI calculations of Hosteny *et al.*[19]). This was then augmented with a diffuse *s*-type Gaussian on the oxygen atom with an exponent of 0.028 and the third set included diffuse *p*-type Gaussian functions on the oxygen atom with the same exponent. The results are summarized in Table III. All other results reported here use the *DZ* + *R* (3*s*, 3*p*) basis.

Omitting the Rydberg functions leads to a 1.05 eV error for the $^3B_1$, 1.49 eV for the $^1B_1$, and 6.33 eV for the $^1A_1$ excitation energies. Goddard and Hunt[10] have calculated $\langle r^2 \rangle$ for the $3sa_1$ orbital from these three states with the following results,

$$\begin{aligned} {}^3B_1\langle r^2\rangle_{3sa_1} &= 17.4\ a_0^2, \\ {}^1B_1\langle r^2\rangle_{3sa_1} &= 21.2\ a_0^2, \\ {}^1A_1\langle r^2\rangle_{3sa_1} &= 25.1\ a_0^2, \end{aligned} \tag{2}$$

in agreement with the trend in the errors in the excitation energies. For the orbitals from higher excited states, $\langle r^2 \rangle = 23\text{–}55\ a_0^2$ implying that the errors would be even more serious if Rydberg character were excluded from the basis set. These results invalidate the claim

TABLE III. The dependence of the CI excitation energies on the basis set.

Basis set	[4*s*2*p*/2*s*]		[4*s*2*p*/2*s*] + *R*(3*s*)		[4*s*2*p*/2*s*] + *R*(3*s*, 3*p*)	
State	E (a.u.)	Δ*E*(eV)	*E*	Δ*E*	*E*	Δ*E*
$^1A_1$ (G.S.)	−76.13563	0.0	−76.13600	0.0	−76.13869	0.0
$^3B_1$ ($1b_1 \rightarrow 3sa_1$)	−75.83014	8.31	−75.86472	7.38	−75.87193	7.26
$^1B_1$ ($1b_1 \rightarrow 3sa_1$)	−75.80120	9.10	−75.85028	7.77	−75.85907	7.61
$^1A_1$ ($3a_1 \rightarrow 3sa_1$)	−75.54225	16.15	−75.72492	11.19	−75.77764	9.82

by Claydon *et al.*[11] that radially expanded orbitals are not needed for the excited states of H_2O.

Since the results of Table I include electron correlation, it is clear that the inclusion of correlation cannot compensate or correct for the lack of diffuse functions. In fact since the correlation energy errors for the $^{1,3}B_1$ states are ~1.2 eV (see Table I) and the error due to the neglect of Rydberg character is comparable but *opposite* in sign, a calculation *without* diffuse functions and *without* electron correlation could benefit from a fortuitous cancellation of errors. However, because the radial extent of the excited orbital varies considerably from state to state, it is not possible to obtain a consistent cancellation. This may explain the sporadic agreement between semiempirical calculations and experiment, and argues against the reasoning of Ho *et al.*[35] that minimal basis set INDO calculations are capable of correctly placing excited states because they incorporate experimental atomic information in the integral approximations. A detailed comparison of the results of *ab initio* and INDO calculations of correlated wavefunctions has been made by Wadt and Goddard.[36]

B. Comparison of Hartree-Fock type calculations

1. Ab initio SCF

From Tables I and IV we see that the HF excitation energies from the $1b_1$ orbital are about 1.2 eV lower than the CI excitation energy. This is also the error in the HF ionization potential (I.P.) and represents essentially the extra correlation energy of the additional doubly occupied orbital of the ground state (as compared with the positive ion or Rydberg excited state). On the other hand, use of Koopmans theorem leads to an I.P. about 1.26 eV *higher* than the experimental energy, indicating a total error in the description of the ion of ~2.5 eV. This results from contraction and readjustment of the orbitals.

The corresponding correlation errors for excitation from the $3a_1$ orbital range from 1.1 to 1.5 eV. Of course for states that are not the lowest of their symmetry type, the HF results are not constrained to be upper bounds. For the $^3B_1(b_1 \rightarrow 3pa_1)$ and $^3A_1(3a_1 \rightarrow 3pa_1)$ states, the solutions collapsed to lower states of the same symmetry and no attempt was made to force convergence to the correct HF wavefunctions.

2. IVO

In contrast the IVO method (Hunt and Goddard[9,10]) obtains variationally correct HF excited orbitals within the approximation that the core orbitals remain the same as in the ground state. In this case one obtains rigorous upper bounds on each excited state. The correlation errors and core relaxation are accounted for by referencing the computed stabilities of the excited orbitals to the experimental ionization potentials. Table IV contains the results of IVO calculations for the sixteen excited states with the same Rydberg basis set used for the HF and CI calculations.

The assumption in the IVO approach[9,10] is that the energy of the excited (Rydberg) orbital is not seriously dependent on the readjustment and contraction of the ground state orbitals. Thus, instead of an SCF calculation on each state only one matrix diagonalization is carried out for each orbital to be ionized, obtaining in each case the whole sequence of excited states (allowed by the basis). Thus in the IVO method only the orbital energy (ϵ) of the excited orbital is calculated, and to obtain excitation energies, ϵ must be added to the I.P.

TABLE IV. Comparison of calculated excitation energies (in eV) of H_2O.

	Upper state	Best estimate[a]	Present work CI	Present work IVO	Present work HF	Goddard Hunt[b] IVO	Yeager McKoy[f] RPA	Yeager, McKoy, Segal[c,f] EOM	Claydon, Segal, Taylor[d] INDO	Boring Wood *et al.* $X\alpha$[e]
$b_1 \rightarrow 3sa_1$	$^3B_1$	7.14	7.26	6.62	6.00	6.68	8.05	6.89	6.20	8.82
	$^1B_1$	7.49	7.61	7.27	6.37	7.30	8.81	7.22	7.43	8.93
$b_1 \rightarrow 3pb_2$	$^3A_2$	9.1	9.34	8.79	8.10	8.68	10.28	8.97	7.49	
	$^1A_2$	9.2	9.46	9.13	8.23	9.04	10.63	9.02	8.03	
$b_1 \rightarrow 3pb_1$	$^3A_1$	9.81	9.74	9.71	8.57	9.70	10.89	9.39		10.52
	$^1A_1$	10.17	10.16	10.38	8.64	10.16	11.64	9.61		10.65
$b_1 \rightarrow 3pa_1$	$^3B_1$	9.93	9.99	10.03		9.96	11.26	9.47		10.50
	$^1B_1$	10.00	10.06	10.14	8.91	10.04	11.39	9.48		10.63
$3a_1 \rightarrow 3sa_1$	$^3A_1$	9.35	9.44	8.97	8.12	9.02	10.16	9.34	8.67	
	$^1A_1$	9.73	9.82	9.85	8.44	9.92	11.10	9.54	10.85	
$3a_1 \rightarrow 3pb_2$	$^3B_2$	11.1	11.11	10.88	10.04	10.81	12.01	11.47	9.43	
	$^1B_2$	11.4	11.47	11.52	10.24	11.46	12.90	11.40	11.06	
$3a_1 \rightarrow 3pb_1$	$^3B_1$	11.9	11.87	12.01	10.63	12.01	...	...		
	$^1B_1$	11.9	11.92	12.10	10.66	12.07	...	...		
$3a_1 \rightarrow 3pa_1$	$^3A_1$	11.8	11.77	11.86		11.85	12.97	11.69		
	$^1A_1$	12.1	12.08	12.49	10.63	12.55	13.55	11.82		

[a]Table II.
[b]Reference 10.
[c]Reference 16.
[d]Reference 11.
[e]Reference 37.
[f]Private communication.

from experiment or from another more accurate calculation.

Comparing the IVO results here with those by Goddard and Hunt[10] using a more extensive basis set, we find agreement to within 0.1 eV in each case, indicating that a single $3s+3p$ set is sufficient for these states. Comparing the IVO and CI results in Table IV we see that the worst cases are $^3B_1(1b_1 \rightarrow 3sa_1)$ leading to an error of -0.64 eV, $^3A_2(1b_1 \rightarrow 3pb_2)$ leading to an error of -0.55 eV, and the corresponding singlets with errors of -0.34 and -0.33 eV. Except for $^3A_1(3a_1 \rightarrow 3sa_1)$ with an error of -0.47 eV, the other states below 11.9 eV lead to errors of $+0.24$ to -0.23. The states with the largest errors involve either an excited $3sa_1$ or $3pb_2$ orbital; these are just the symmetries of the OH antibonding orbitals. As a result one expects some additional valence character in the Rydberg orbitals (clearly indicated in the orbital sizes[10]). To whatever extent the excited state is valence-like one can expect the correlation error to differ from that of the ion and hence an error in the IVO excitation energy.

3. $X\alpha$

An approximate method of carrying out calculations of Hartree–Fock-type wavefunctions has been proposed in which the exchange terms are replaced by potentials proportional to $\rho^{1/3}$ and the potentials are simplified to a muffin tin form.[37]

Boling *et al.*[38] carried out self-consistent $X\alpha$ calculations on H_2O obtaining the results in Table IV. Except for the above approximations (and some additional approximations in dealing with spin symmetries), these results should reproduce the *ab initio* HF results. Thus the errors intrinsic to the $X\alpha$ procedure lead to disagreements of 1.7 to 2.8 eV, all high.

The problem with $X\alpha$ is apparently not in the description of the diffuse Rydberg orbital since the calculated I.P. for the excited (Rydberg) orbitals is generally within 0.2 eV of the IVO result (except for $1b_1 \rightarrow 3sa_1$ where the $3sa_1$ orbital is calculated with $X\alpha$ to be 1.2 eV higher than the IVO orbital). Rather, the difficulty seems to lie in the $X\alpha$ description of ionization. *Ab initio* wavefunctions lead to an I.P. from the $1b_1$ orbital of 13.88 eV using Koopmans theorem (frozen orbitals) and 11.4 eV using SCF orbitals for the ion. Although the $X\alpha$ method involves solving self-consistently for the ion orbitals, the resulting I.P. is 13.39 eV, only slightly better than the frozen orbital or Koopmans theorem values. In an *ab initio* calculation such an error would be expected from using a minimal basis set with a scale chosen for the neutral system.

4. INDO

The INDO method corresponds to carrying out Hartree–Fock calculations in which most of the basic molecular integrals are neglected and many others are evaluated empirically. These approximations were developed for closed shell wavefunctions and lead to a relatively good cancellation of errors for such systems.[36] For the excited states the Coulomb and exchange integrals no longer occur in the combination $2J-K$ and larger errors are found.[39] A second difficulty equally important for water is that the INDO calculations use only a minimal basis of valence-like Slater orbitals. As shown here and by Goddard and Hunt,[10] all the excited states involve a diffuse orbital.

In the INDO calculations there are only two empty orbitals available for occupation, $4a_1$ and $2b_2$, and hence only a few excited states are allowed.

The most consistent comparison is between INDO and the *ab initio* HF calculations since the INDO approximation was developed to approximate HF wavefunctions. From Table IV we see that the errors are $+0.20$, $+1.06$, -0.61, -0.20, $+0.55$, $+2.41$, -0.61, and $+0.82$ eV for the states allowed in INDO. These are surprisingly low errors given the severity of the approximations.

Occasionally it is hoped that somehow the errors in the INDO approximation will balance the correlation errors in HF wavefunctions so that the INDO results will agree with experiment.[11,35] From Table IV we see that INDO and the best estimates of ΔE differ by -0.94, -0.06, -1.6, -1.2, -0.68, $+1.12$, $+1.7$, and $+0.3$ eV, a range of $+1.7$ to -1.6, slightly larger than the range of errors between INDO and HF. It is interesting to note that the only state with a very small error (0.06 eV) is $1b_1 \rightarrow 3sa_1$, the best known of the states considered.

Thus comparing INDO with HF or INDO with experiment, the errors in excitation energy fluctuate over a range of greater than 3 eV. This is large compared with the spacing of the excited states and hence one cannot expect the INDO results to provide much help in elucidating the nature or assignments of the excited states.

Realizing the large errors inherent in the INDO procedure, Clyadon, Segal, and Taylor (CST)[11] attempted to combine INDO results with experimental data to explain various experimental phenomena. Their interpretations were:

(a) Both $^1B_2(3a_1 \rightarrow 2b_2)$ and $^1A_1(3a_1 \rightarrow 4a_1)$ are degenerate in the Franck–Condon region and are both responsible for the broad 8.7–10.0 eV absorption, both leading to OH $(A^2\Sigma^+) + H(^2S)$ for $E > 9.13$. The double peak in the rotation distribution of OH $(A^2\Sigma^+)$ is due to the excitation of two dissociative states.

(b) A low intensity feature observed at 6.5 eV energy loss for 50 eV electrons and absent in ultraviolet spectra is consistent with electric quadrupole allowed excitation of the $^1A_2$ state.

(c) The lowest triplet state $^3B_1$ has a term value, T_0 of ~4.0 eV.

(d) The $^3A_1$ and $^3B_2$ states are predicted to yield a double-peaked rotational distribution of OH $(A^2\Sigma^+)$ in photosensitized decomposition of H_2O.

A crucial point in (a) above was the near degeneracy of the $^1B_2$ and B^1A_1 states (the INDO calculation gives a separation of 0.21 eV). However it is now clear that the separation of these states is 1.7 eV (INDO was high

by 1.1 eV for $^1A_1$ and low by 0.4 for $^1B_2$). Thus the whole interpretation of (a) is wrong.

In (b) CST obtained an INDO energy of 8.03 eV for $^1A_2$ and assumed that the INDO energy is too high by about 1.5 eV. In fact the INDO calculation was too *low* by about 1.5 eV. As a result CST interpret a feature at 6.5 eV as due to $^1A_2$ when in fact this state is found at 9.46 eV.

Concerning point (c), CST calculated a vertical excitation energy of 6.20 eV to the $^3B_1$ state and an adiabatic excitation energy of 4.76 eV. They assumed that the INDO results are 1 eV too high and that the $^3B_1$ state was responsible for the 4–5 eV feature observed in electron impact. However the INDO results were in fact 1 eV too low (as is now well established by our CI calculations). A second error resulting from the modified INDO results is that the $^3B_1$ state was thought to be strongly bound ($\sim$1.4 eV) with respect to OH ($^2\Pi$)+H(^2S). In fact, extensive MC–SCF calculations over the whole grid of geometries by Hosteny *et al.*[15] show the $^3B_1$ state to be repulsive. (Earlier, less extensive *ab initio* calculations by Miller *et al.*[12] had also indicated the $^3B_1$ state to be repulsive.)

There is no experimental evidence for or against point (d) above. However, the CI calculations indicate that the $^3A_1$ and $^3B_2$ states are separated by 1.7 eV so that there is no longer any basis for CST's predictions. We calculate three states near 9.4 eV [$^{3,1}A_2(b_1-3pb_2)$ and $^3A_1(3a_1-3sa_1)$] separated by only 0.1 eV, perhaps explaining the experimental results.

5. Configuration interaction

No other comprehensive CI calculations on the excited states of H_2O have been reported.[40] *Ab initio* CI calculations have been reported for selected states. The ground state has received considerable attention with the calculations of Schaefer and Bender,[20] Hosteny *et al.*,[19] and the recent work of Rosenberg.[21] Hosteny and co-workers[15] have used the multiconfiguration SCF(MC–SCF) method to investigate the potential surface for the lowest $^3B_1$ state. They used the 4–31 G basis of Pople augmented with diffuse s and p functions. Due to the smaller basis set their HF energies for the X^1A_1 and A^1B_1 states were inferior to those presented here (−75.9126 a.u. compared to −76.0111 a.u. for $^1A_1$ and −75.6920 a.u. compared to −75.7908 a.u. for $^3B_1$). However the HF excitation energy is 6.0 eV in both cases. Their MC–SCF energy is also less accurate than our CI results (−75.7152 a.u. compared to −75.8719 a.u.); the energy lowering for the MC–SCF calculation is only 0.6 eV compared with 2.2 eV for the CI calculation. The calculations of Hosteny *et al.*[15] were designed to investigate the nature of the potential surface for the $^3B_1$ state and they did not report an MC–SCF energy for the $^1A_1$ state.

6. Approximate CI

Yeager *et al.*[16] have reported approximate CI calculations on ten of the excited states of H_2O using the Random Phase Approximation (RPA) and higher RPA (HRPA) approximation to the Equations of Motion (EOM) method in which excitation energies are solved for directly.

The RPA approach uses a one particle–one hole ($1p$-$1h$) excitation operator and formally includes double excitations in the ground state wavefunction; however, the correlation terms are omitted from the equations of motion. The HRPA approach includes the correlation terms to first-order and includes approximately (using perturbation theory) the two particle-two hole ($2p$-$2h$) terms in the excitation operator. Assuming that HRPA is a close approximation to the full EOM solution, HRPA is often just denoted as EOM.

From Table IV it is clear that the RPA overestimates the excitation energies by 0.8–1.5 eV. This is not surprising considering that the ground and excited states do not include the same degree of electron correlation. Obviously the RPA method would not provide a reliable basis for the assignment of the states of H_2O.

The EOM approach allows double excitations from the ground *and* excited configurations but includes these terms in an approximate way (using perturbation theory). Comparing the EOM and *ab initio* CI results we find errors of −0.37, −0.39, −0.37, −0.44, −0.35, −0.55, −0.52, −0.58, −0.10, and −0.28 eV, respectively. Thus it appears that the EOM approach leads to a systematic error, underestimating the $1b_1$ excitations by $\sim$0.4 to 0.6 eV.

Yeager *et al.*[16] assigned several transitions not previously identified by experimentalists. Their conclusions can be summarized as follows:

(a) The $^3B_1$ state is responsible for the strong feature at 7.2 eV in electron impact. Their calculated ΔE of 6.9 eV was in agreement with the earlier IVO calculations[10a,10b] (6.6 and 6.7 eV).

(b) The 9.81 eV feature is probably due to $^3A_1$ or $^3B_1$. Hunt and Goddard[10] had earlier assigned this as $^3A_1$ as we have in this paper.

(c) The 9.1 eV feature is due to the $^1A_2$ state. Our conclusion is that the 9.1 eV feature is actually due to $^3A_2$.

Yeager *et al.*[15] also agreed with the earlier findings of Hunt and Goddard[10] and of Hosteny *et al.*[15] that the $^3B_1$ state of H_2O is not responsible for the 4.5 eV feature observed in electron impact.[1]

V. SUMMARY

The results presented here represent the most accurate and detailed study of the excited states of H_2O to date. The calculations have corrected some misconceptions concerning the excited states and have provided the first reliable energies for several transitions. The Rydberg nature of the excited states has been demonstrated to persist when electron correlation is included in the description. The results have provided a useful comparison between several approximate methods (IVO, INDO, etc.) and *ab initio* calculations on the excited states. In general the IVO method has been shown to be a reliable and a reasonably accurate method for making state assingments. The INDO and $X\alpha$ semiempirical methods have been shown to be of questionable value.

The importance of including polarization functions in the basis set and the subsequent effect on the excited states has not been determined. This will be the subject of a future study as will be the potential surfaces of the excited states of H_2O.

ACKNOWLEDGMENTS

The authors wish to thank Dr. S. Trajmar, Dr. A. Chutjian, and Dr. R. Hall for many helpful discussions and for making their experimental results available prior to publication. The programming assistance of Ms. J. Frawley is also gratefully acknowledged.

*Supported by a grant (PF-042) from the President's Fund of Caltech.

†Partially supported by a grant (GP-40783X) from the National Science Foundation.

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§Contribution No. 5025.

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